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THERMOANALYTICAL AND MASS SPECTROMETRIC STUDIES ON VOLATILE β-DIKETONE CHELATES

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SUMMARY

Thd-chelates (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) of Y, Ce, Pr, Sm, Eu, Gd, Tb, Tm and Yb and hexafluoroacetylacetonates (hfa) of Pr and Eu were studied by TG, DSC and MS techniques. TG and DSC curves of the complexes indicated the sublimation between 100 and 300 °C. According to the DSC measurements the sublimation temperatures of rare earth thd chelates decrease with the cation size being 223 °C for Pr and 170 °C for Yb. The sublimation temperatures of fluorine containing complexes were 100 degrees lower than those of thd-chelates.

The mass spectra of the rare earth-thd chelates were very similar. The main peak in each spectrum corresponded $Ln(thd)_2$. The alkaline earth-thd chelates exist as $M_2(thd)_3$ species in the UHV conditions. The strongest peaks in the MS of the fluorocomplexes were the following: $Pr(hfa)_3 \cdot H_2O$ and $Eu(hfa)_3 \cdot DMF$.

INTRODUCTION

Volatile metal chelates have been used for the gas-chromatographic separation of metals, in particular rare earths whose separation by other means is difficult (refs. 1-4). A more recent application of volatile metal chelates is their use as source materials in the growth of thin films by chemical vapor deposition (CVD) processes (refs. 5-7).

Alkaline earth and rare earth metals have only a few volatile compounds which can be used in CVD deposition of thin films. β-diketonate complexes of these elements are volatile and sufficiently stable and therefore they have been applied in the CVD growth of high T_c superconducting films, for instance (refs. 5,6). β-diketone chelates have also been succesfully employed by us in the growth of semiconductor layers for electroluminescent thin film devices by the Atomic Layer Epitaxy process (ALE) (refs. 8-11). In the present paper TG, DSC and MS data will be presented for selected β-diketonate complexes. The data obtained are useful interpretation of the behaviour of β-diketonate chelates in ALE thin film growth. Furthermore, they contribute to a better understanding of the film growth processes from the gas phase.

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EXPERIMENTAL

Synthesis of Metal Chelates

The ligands (2,2,6,6-tetramethyl-3,5-heptanedione = thd, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione=hfa), alkaline earth nitrates as well as the rare earth oxides were commercial, analytically pure reagents. The metal chelates studied were synthesized following the methods documented in the literature: $M(thd)_2$ (M = Ca,Sr,Ba) (ref.12), $Ln(thd)_3$ (Ln = Y,Ce,Pr,Sm,Eu,Gd,Tb,Tm,Yb) (ref.13), $Ln(hfa)_3 \cdot nH_2O$ (ref.14).

Thermogravimetry and Differential Scanning Calorimetry

Thermoanalytical measurements were carried out by the Perkin-Elmer Series 7 instruments. The sample size in TG measurements was about ten milligrams and in DSC measurements five milligrams. The heating rate was 10 °C/min in all measurements. Dry argon was used as flow gas.

Mass Spectometry

The molecular formula of the volatilized species were determined in a VG 7070E high-resolution mass spectrometer which has a heated inlet for solid samples. The temperature of the sample chamber was in the range 250-400 °C.

RESULTS AND DISCUSSION

The results obtained in the TG and DSC measurements are summarized in Table 1 which also gives the colors of studied materials.

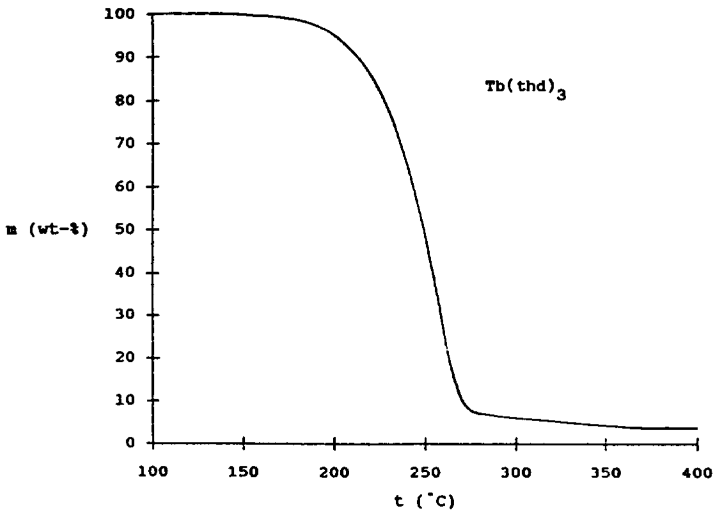

Fig. 1. A typical TG curve for $Tb(thd)_3$.

TABLE 1

Sublimation or decomposition temperatures, weight remaining in TGA, DSC peak temperature and color of the chelates.

Compound	Temperature range of sublimation as determined by TG (°C)	Residue wt.-%	DSC peak temperature (°C)	Color of the chelate
$Y(thd)_3$	215-251	1.9	173	white
$Ce(thd)_4$	246-254	1.8	203	brown
$Pr(thd)_3$	249-290	5.3	223	light-green
$Sm(thd)_3$	232-274	1.2	205	white
$Eu(thd)_3$	229-266	2.0	192	yellow
$Gd(thd)_3$	225-254	7	186	white
$Tb(thd)_3$	222-257	3.3	182	white
$Tm(thd)_3$	217-245	2.9	174	white
$Yb(thd)_3$	216-250	1.2	170	white
$Ca(thd)_2$	284-309	5.0		white
$Sr(thd)_2$	303-336	6.5		white
$Ba(thd)_2$	349-403	6.9		white
$Pr(hfa)_3 \cdot 3H_2O$	230-260	17.0	124	light-green
$Eu(hfa)_3 \cdot H_2O \cdot DMF$	190-231	9	84	light-pink

All the rare earth thd complexes show in TG studies similar behaviour. Their TG curve is smooth and the weight loss is rapid and complete approaching 100 percent. Fig.1 shows a typical thermogram for a rare earth thd complex. When the radius of the trivalent rare earth ion decreases, the volatility of the chelates increases (ref. 15). The size of yttrium is close to that of ytterbium and accordingly their thd chelates sublime in the same temperature range.

The alkaline earth thd complexes have similar TG curves showing only sublimation with complete weight loss. The volatility decreases in the series Ca>Sr>Ba. The tendency is the same as found in rare earth complexes: the smaller the cation the better the volatility.

As expected, the fluorine substituted chelates have greater volatility than the non-fluorine substituted species (Table 1)(ref. 16). Fluorinated acetylacetonates have incomplete coordination (ref. 17) and they fill the coordination sphere in aqueous solutions by aqua ligands. Upon heating these complexes do not sublimate completely but partial decomposition occurs. The

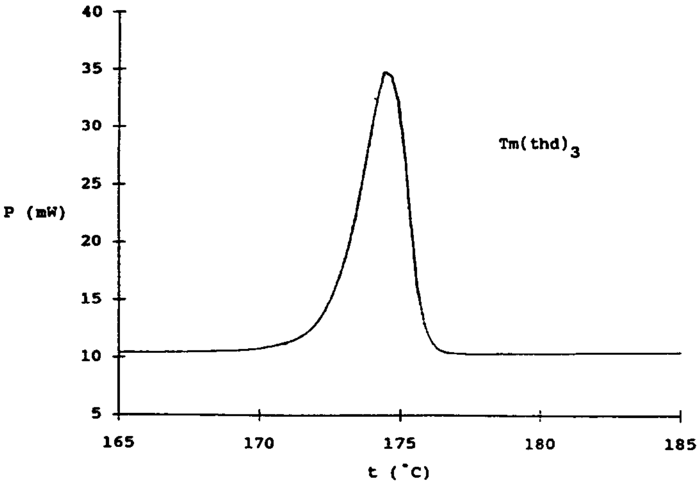

Fig. 2. A typical DSC curve for Tm(thd)$_3$.

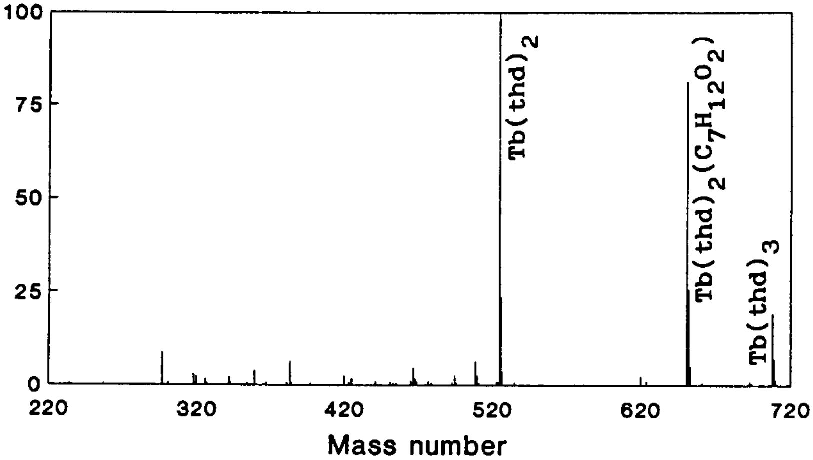

Fig. 3. The high resolution mass spectrum of Ln(thd)$_3$.

volatility can be improved by the substitution of aqua ligands by dimethylformamide (DMF) or tri-n-butylphosphinoxide (ref. 18).

A typical DSC curve is shown in Fig. 2. The curve contains only an endothermic peak which is due to the sublimation of the thd chelate. All the rare earth thd and hfa chelates studied showed a similar behaviour. The sublimation temperatures exhibit the same trend as found in TG curves: the temperature decreases with decreasing cation size (Table 1). $Pr(hfa)_3 \cdot 3H_2O$ showed an endothermic peak at 124 °C and an exothermic peak at 295 °C indicating that some decomposition takes place.

In the mass spectra of rare earth thd chelates the main peaks correspond to molecules with stoichiometry of $Ln(thd)_2$ (Fig. 3). The molecular peak $Ln(thd)_3$ can be found in the spectra as well as Ln(thd) together with several decomposition fragments of the ligand. The mass spectra of fluorine-substituted acetylacetone chelates of rare earths are more complex. Suprising is that the "extra" ligands, water in $Pr(hfa)_3$ and DMF in $Eu(hfa)_3$, are so strongly bound that they remain in the complexes in the gas phase (Fig. 4). In alkaline earth thd chelates the molecular peaks correspond to the formula $M_2(thd)_3$ (Fig. 5). The presence of this molecule has earlier been documented in the literature (ref. 20). The other noteworthy peak in the spectrum is that of M(thd). It is interesting to note that for a chelate mixture consisting of $Ca(thd)_2$ and $Sr(thd)_2$ heteronuclear species in the form of $CaSr(thd)_3$ have been detected by a mass spectrometric study (ref. 19)

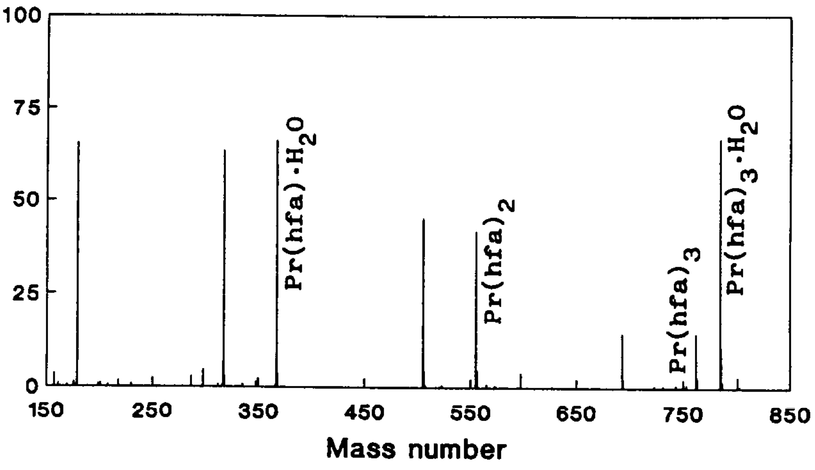

Fig. 4. The mass spectrum of $Pr(hfa)_3 \cdot 3H_2O$.

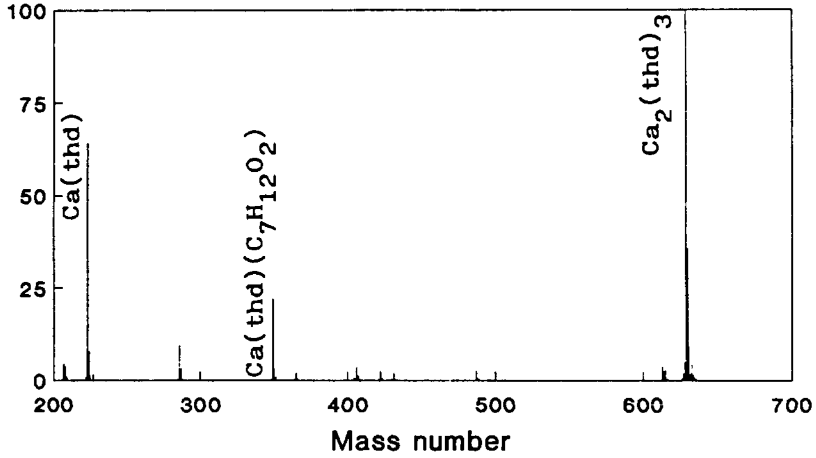

Fig. 5. The mass spectrum of $Ca(thd)_2$.

Our previous studies on ALE deposition of MS (M = Ca,Sr,Ba) films doped with Ln^{3+} ions have shown that polycrystalline highly luminescent materials can be obtained using thd chelates as sources. A typical feature for ALE deposited films grown from elements or small molecules is a strong preferential orientation towards a certain crystal direction (ref. 20). In the case of $M(thd)_2$ the growth rate of the films is slow and the preferential orientation is not perfect. The low growth rate means that the large thd ligands remain coordinated when the $M(thd)_x$ gaseous species are chemisorbed on the substrate. Due to the steric hindrance the coverage of metal atoms on the surface is low.

The MS results indicate that alkaline earth metals are entering the growing surface bound in different species. This may affect the films to orientate differently at different sites of the substrate. The share of different $M(thd)_x$ species in the gas mixture may vary depending on the experimental conditions. This results in differently oriented films if growth conditions vary.

CONCLUSIONS

The TG and DSC measurements showed that the β-diketonate chelates of alkaline earth and rare earth metals sublime easily in inert atmosphere. The sublimation temperature depends on the cation size of the metal. According to the mass spectra the gas phase generated by sublimation is a complex mixture of species where different ligand to metal ratios can be found.

Thermoanalytical methods are useful means for studying volatile compounds for possible use in the CVD growth of thin films. The sublimation temperatures and the completeness of the sublimation can be measured. A mass spectrometer can be utilized in studying the composition of species in the gas phase. However, the mass spectrometer is an UHV instrument and thus the results are not directly comparable to those found in thin film deposition equipment. The MS results, however, give an indication on which complexes may exist in the gas phase and contribute to a better understanding of the reaction mechanisms during the film growth. In the case of β-diketonate chelates the gas phase contains a mixture of species leading obviously to a very complex film growth process.

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